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Sampling and Analysis Methods for Use in Source Apportionment Studies to Determine Impact of Wood Burning of Fine Particle Mass

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SAMPLING AND ANALYSIS METHODS FOR USE IN SOURCE APPORTIONMENT STUDIES TO DETERMINE IMPACT OF WOOD BURNING ON FINE PARTICLE MASS

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Aerosol sampling and analysis procedures are described which may be used to obtain ambient air measurements for input into source apportionment studies to estimate the impact of wood burning on ambient particulate loadings. Ambient wintertime fine particle compositions in Denver, CO, and Albuquerque, NM, are used as examples for receptor model calculations.

Introduction

Recent increases in the use of wood as an energy source have reintroduced an old wintertime air quality problem to suburban areas of the United States. This problem is principally related to visibility degradation. Atmospheric visibility can be substantially degraded by the fine particle (< 2.5 μm aerodynamic diameter) emissions that are formed during the combustion of wood or wood products. The chemical and physical characteristics of these emissions that impact the environment are well documented in a recent conference proceedings published by the Oregon Graduate Center (Cooper and Malek, 1982).

This article describes air pollution monitoring procedures that would lead to development of a receptor modeling data base to be used for determining the magnitude of wood-burning emissions and the extent to which they affect ambient particulate loadings and visibility. A diagram of these procedures is shown in Fig. 1. However, before an air monitoring project to gather data for receptor modeling is implemented, existing air quality and emission information should be examined and put into available air quality dispersion models to estimate the relative magnitude of the pollution problem due to major emission sources in the airshed. Recently, Dennis (1983) of the National Center for Atmospheric Research prepared a report projecting the impact of major emission sources on particulate loadings in Denver over the next 20 years using an emissions inventory/dispersion approach. He found wood burning to be one of the important sources.

Receptor modeling is best applied in conjunction with other forms of air quality modeling, such as the approach used by Dennis (1983), where he used receptor modeling results from Denver, CO, to complement results of air dispersion models for the same airshed. Receptor modeling provides an assessment of the sources presently contributing to particulate loadings at a given site, which is independent of dispersion modeling results. Thus, it can lend credibility to the results and projections of dispersion models which are needed to assess both the trends in particulate loading and the effectiveness of possible control strategies.

Discussion

Receptor Model

A receptor model is a mathematical method for identifying and quantifying the sources of ambient air contaminants at a receptor, primarily on the basis of concentration measurements made at the receptor. Receptor modeling can reasonably address the issue of source apportionment because the source signature of wood burning emissions contain % levels of fine particle potassium, which in many urban atmospheres can serve as a unique tracer. Typically, ambient levels of fine particle K rarely exceed 0.1 $\mu g/m^3$. Therefore, during the winter when K exceeds 0.1 $\mu g/m^3$, these events can often be associated with wood burning emissions.

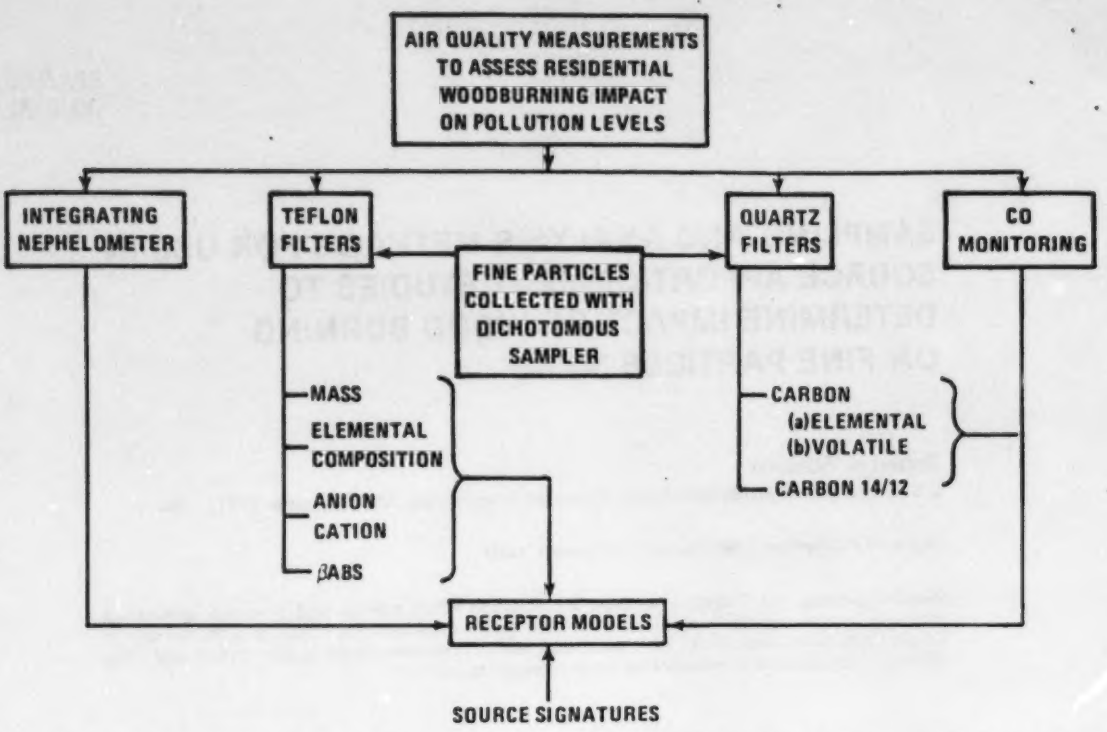

Fig. 1. Flow diagram of sampling and analysis needed to support receptor modeling related to residential wood burning. (See Table 2 for definitions of abbreviations.)

The formulation of all receptor-based models for particle source apportionment is based on the assumption that the primary emissions of all species, including the tracer from a given source, are transported to the receptor site in an identical manner. Thus, if a number of sources, p, exists, and if there is no change in the ratio of the tracer species and the companion primary emissions, the total airborne particulate mass measured at the receptor, C, will be a linear sum of the contributions of the individual sources S_j:

$$C = \sum_{j=1}^{p} S_j. \tag{1}$$

Similarly, for species or property i, the mass concentration C_i, will be

$$C_i = \sum_{j=1}^{p} a_{ij} S_j. \tag{2}$$

where a_{ij} is the mass fraction of source contribution j, possessing property i at the receptor.

Cooper and Malek (1982) has described one type of receptor modeling study dealing with source apportionment of wood-burning emissions in a vegetative burning study (i.e., burning of residual agricultural products) conducted in Oregon. Since that time, a number of improvements in gathering air quality data have occurred. This report presents several source apportionment procedures that incorporate these improvements. It describes sampling at the source and at the receptor site, the analytical procedures applied to the samples, and the use of receptor models in assessing the impact of wood burning on the ambient particulate loading.

Source Signatures of Wood-Burning Emissions and Related Measurements

Before a receptor modeling study is initiated, it is advisable to obtain source signatures associated with the wood being used in the air shed under study. Woodstove emission characteristics have been studied extensively over the past few years by a number of investigators, such as Lamason (1982) and DeAngelis *et al.* (1980). The major emissions from wood burning, in decreasing order of concentration, are carbon monoxide, volatile hydrocarbons, particulate matter, and oxides of nitrogen. The particles are composed, again in decreasing order of concentration, of volatile organic compounds, elemental or soot carbon, and inorganic compounds. Most of the emission factors reported in the literature for wood stoves have been obtained using sample collection apparatus similar to the one shown in Fig. 2 and described by Osborne (1982). This apparatus uses all of the features of the U.S. Environmental Pro-

tection Agency's (U.S. EPA) Method 5 for source sampling, including a trap to collect volatile organic compounds. In some studies, oxides of nitrogen and carbon monoxide content of flue gas emissions from wood stoves are monitored as shown in Fig. 2.

The carbon monoxide emissions from wood burning are also significant. Table 1 contains the emission factors for particulate matter and carbon monoxide obtained by Butcher and Ellenbecker (1982) in their studies on wood-stove emissions. In the studies by Lamason (1982), carbon monoxide emissions from wood stoves were found to be significantly higher than from residential fireplaces.

DeCesar and Cooper (1982) studied the relative ratio of the total carbon emissions to elemental emissions in size-fractionated wood-burning emissions as a function of wood type and burning conditions. In their studies, potassium averaged 1% of the fine particle mass from emissions of pine wood burned in fireplaces and wood stoves.

The majority of the emissions from wood burning are in the fine fraction, and they are largely composed of organics with low vapor pressures and soot carbon. These are the species that generally have the most impact on visual air quality. For this reason, a sampling and analysis procedure was developed that collected, primarily, the fine fraction of wood-burning emissions.

This U.S. EPA study, conducted by Stiles (1983) determined the relative emission characteristics of soft and hard woods burned in a commercially available wood stove. Figure 3 shows the relative amounts of inorganics and carbon emitted from pine, oak, and sweet gum woods during the middle stage of burning, which was representative of the emissions for the complete burn cycle. The carbon emissions are divided into two general classes: elemental carbon and volatile carbon. This classification is based on the properties of the carbon emissions exhibited during analyses. Specifically, during the analysis of quartz filters using the procedure of Stevens *et al.* (1982), the volatile carbon fractions

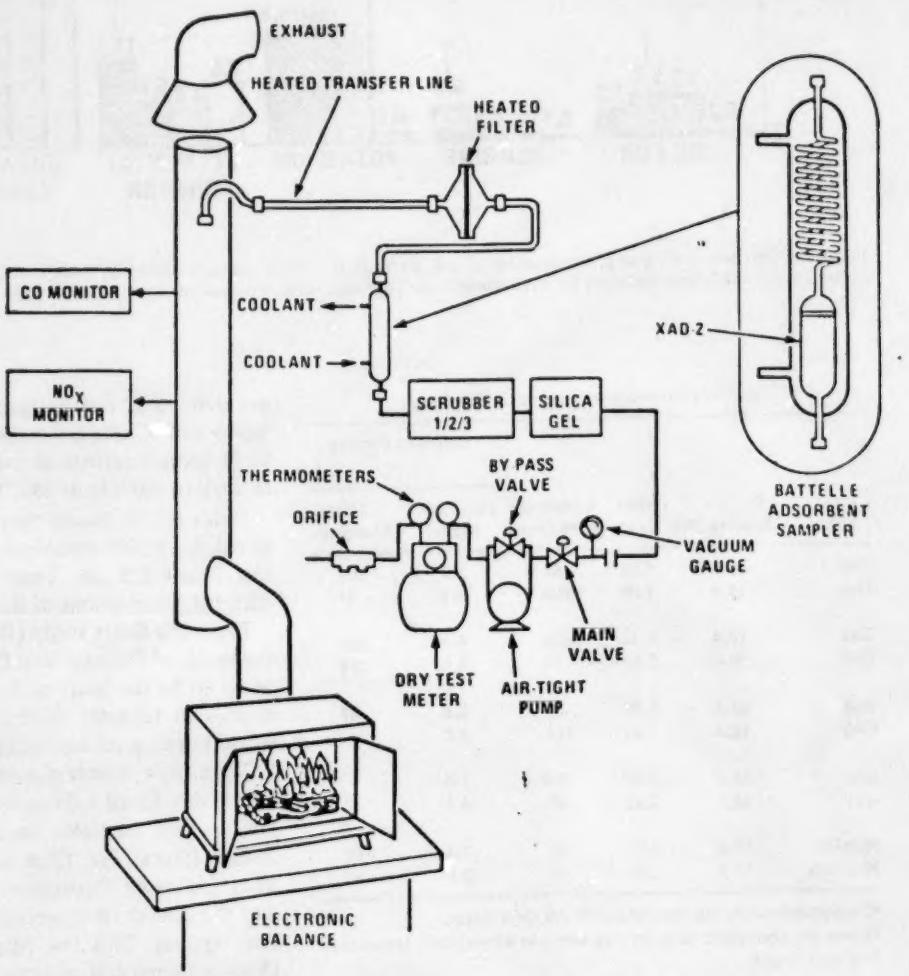

Fig. 2. Diagram of a typical wood-stove emission monitoring and sampling arrangement.

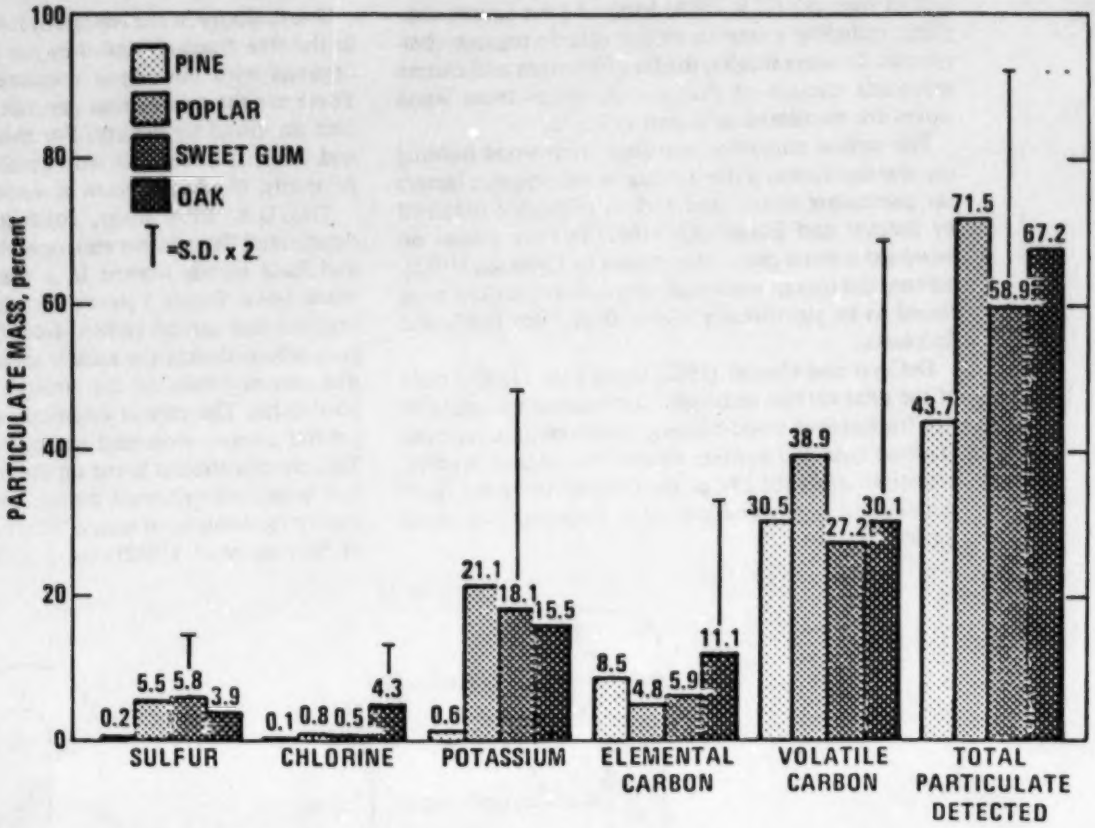

Fig. 3. Comparison of the particulate emission of oak, sweet gum, poplar, and pine during the middle stage of burning. The standard deviation shown are for the largest variation for each wood type. Typically, three observations were made for each wood class.

Table 1. Emission factor summary for wood.

Wood	Moisture (%)	Mass (kg)	Length of Burn (min)	Emission Factors (g/kg) Particulate Matter	Carbon Monoxide
Oak	18.4%	3.09	61	3.9	106
Oak	18.4	3.09	108	4.3	63
Oak	18.4	4.26	123	6.4	106
Oak	18.4	2.67	74	3.2	158
Oak	16.4	2.89	60	2.6	67
Oak	16.4	3.26	114	3.8	[a]
Oak	16.4	0.88[b]	24[b]	1.6	[a]
Oak	12.7	2.52	67	4.2	[a]
Hemlock	15.9	2.52	45	2.4	98
Hemlock	15.9	2.86	56	2.1	[a]

[a]Carbon monoxide was not measured for these burns.
[b]These are aggregated data for two burns in which small amounts of fuel were added.

are defined as those organic materials that are volatile below 650 °C and the elemental carbon fraction (mostly black soot) is defined as the carbon that can be converted to carbon dioxide at 850 °C in the presence of oxygen.

Stiles (1983) found that 70–80% of the total wood-burning particle emissions have an aerodynamic diameter below 2.5 μm. These observations are consistent with the observations of Butcher and Ellenbecker (1982).

From the Stiles study (1983), as shown in Fig. 3, and the work of DeCesar and Cooper (1982), potassium appears to be the best candidate to be used as the tracer species in receptor modeling to assess the impact of wood burning on air quality.

To obtain source-signature particulate data, Stiles (1983) developed a dilution sampling system that would collect fine particles simultaneously on Teflon and quartz filters. The filter samples on Teflon would be used for x-ray fluoresence (XRF) elemental analysis, and the quartz filter would be used to measure the carbon content. This two-filter system was named the S³ (Source Signature) sampler. The laboratory experimen-

tal S³ sampling apparatus developed by Stiles (1983), used both for sampling method intercomparison experiments and for acquisition of filter samples for chemical analysis, is shown in Fig. 4. A single, airtight wood stove (Ashley model 7150-B) was used for all experiments. The stove was mounted on a floor balance capable of measuring weight differences of 250 g, and the flue and damper assembly were flexibly coupled to the stove to permit periodic monitoring of combustion rate through weight loss. A dilution ratio of clean air to flue gas was generally 6 to 1 during the collection of particle emissions.

Substantial variations in the concentration of potassium and carbon were observed by Stiles (1983) during the burn cycle for different types of wood. For example, potassium concentration from the pine-burning experiment was much lower than for the hard woods. Assuming these low potassium emission values are accurate for pine, then in geographic areas where pine is the principal wood used in stoves and fireplaces, the appropriate potassium to fine particle mass ratio to be used in preliminary receptor calculations would be 1% However, in areas where hard woods are the principal type wood being used, the potassium to total fine mass ratio would be about 18%.

Receptor Modeling Using Wintertime Data Sets from Denver and Albuquerque

In addition to obtaining source signatures for receptor modeling, the elemental composition, if available, of aerosols collected within the airshed of interest should be carefully evaluated. If possible, ambient particles should be separated into fine (<2.5 μm) and coarse (>2.5 μm) fractions with dichotomous samplers over consecutive 12-h periods. These sampling periods should be adjusted so that daytime and nighttime samples can be obtained. For example, samples collected between 7:00 am to 7:00 pm (daytime) and 7:00 pm to 7:00 am (nighttime) during the winter are useful in determining the impact of wood smoke on air quality. This sampling schedule is recommended because during the winter, most residential wood burning occurs at night, while during the day emissions from motor vehicles tend to dominate the fine particle mass (Lewis and Einfeld, 1985).

Table 2 contains data on the aerosol composition of air samples collected by the U.S. EPA in Denver, CO, on 19–20 January 1982, and by Sandia Laboratories in Albuquerque, NM, on 3–4 January 1983. These two cities are similar geographically in that they are both at elevations about 1,200 m and are not highly industri-

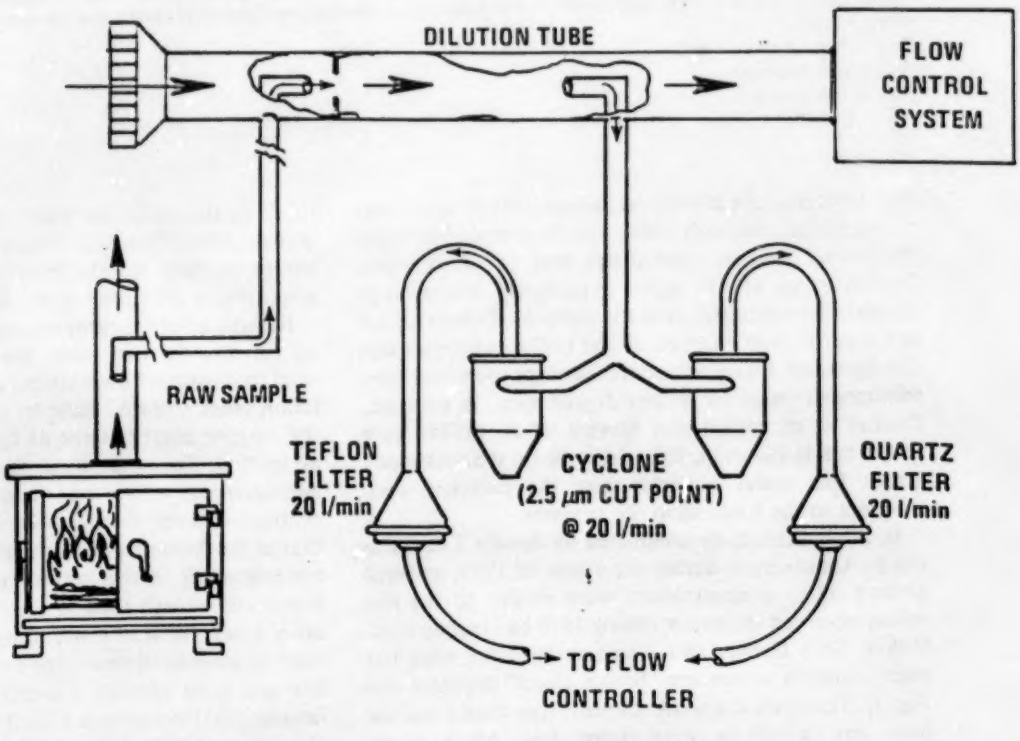

Fig. 4. Schematic of S³ sampling dilution system to obtain fine particle samples during wood burning emission characterization studies.

Table 2. Comparison of wintertime aerosol in $\mu g/m^3$ in Denver, CO, and Albuquerque, NM.

	Denver, CO, 19–20 January 1982				Albuquerque, NM[a] 3–4 January 1983			
	Night		Day		Night		Day	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
	($\mu g/m^3$)							
Mass	35.2	28.2	26.9	29.2	154	16.0	41.0	37.0
Al	0.480	2.710	0.264	2.39	0.275	0.793	0.218	1.450
Si	0.413	6.900	0.247	6.16	0.070	2.14	0.138	3.790
S	1.050	0.230	1.54	0.245	0.737	0.162	0.932	0.293
Cl	0.056	0.636	0.045	1.01	0.165	0.193	0.31	0.948
K	0.118	0.575	0.061	0.510	0.611	0.263	0.113	0.423
Ca	0.059	0.583	0.051	0.531	0.062	0.843	0.780	1.530
V	BD[b]	BD	BD	BD	BD	BD	BD	BD
Mn	0.008	0.016	0.013	0.014	BD	0.008	BD	0.016
Fe	0.098	0.774	0.083	0.733	0.027	0.595	0.057	1.020
Ni	0.003	0.003	0.004	BD	BD	BD	BD	BD
Cu	0.018	0.009	0.012	BD	BD	0.004	0.000	0.005
Zn	0.043	0.020	0.029	0.017	0.039	0.032	0.027	0.055
As	BD	BD	BD	BD	BD	BD	BD	BD
Se	BD	BD	BD	BD	BD	BD	0.002	BD
Br	0.180	0.032	0.122	0.029	0.442	0.098	0.356	0.117
Pb	0.557	0.123	0.428	0.104	1.110	0.371	1.260	0.443
Sn	BD	BD	BD	BD	0.031	0.000	0.003	–
VC[c]	16.4	NM[d]	8.50	NM	75.0	5.0	15.0	2.0
EC[e]	3.23	NM	3.30	NM	15.0	2.0	5.0	1.0
Nitrate	3.40	NM	5.20	NM	9.11	NM	6.27	NM
Sulfate	2.62	0.352	4.64	0.366	2.27	0.84	2.51	1.33

[a]Air quality data collected by Sandia Laboratories (Dr. B. Zak, principal investigator) for the city of Albuquerque. This data set should be considered preliminary, since it is currently undergoing Department of Energy (DOE) quality assurance evaluation. The data were selected for this report to exemplify composition of fine particles in an airshed impacted by wood burning emissions. Data selected for periods when concentration of fine particle carbon at night $\geq 20\ \mu g/m^3$. Nitrate measured in Albuquerque is not total nitrate, but nitrate remaining in fine particle sample after collection.

[b]BD = Below detection level.

[c]VC = volatile carbon.

[d]Nm = Not measured.

[e]EC = elemental carbon.

alized. Neither city is affected substantially by coal-fired power plants, although within the Denver airshed there are several medium-sized plants and an oil refinery. Dzubay *et al.* (1981) report a relatively low average monthly aerosol sulfur concentration for Denver of 0.4 to 1.0 $\mu g/m^3$ over a period of 1 yr (1979), which implies that local and distant SO_2 sources are not the major contributors to visual air quality degradation. In contrast, Dzubay *et al.* (1982) and Stevens *et al.* (1984) have shown that in Houston, TX, and in the rural Shenandoah Valley fine sulfur particles were the principal contributors to the haziness in the summer.

In the limited study conducted by Sandia Laboratories in Albuquerque during the winter of 1983, ambient aerosol sulfur concentrations were similar to the low values observed in Denver during 1979 by Dzubay *et al.* (1981). Both Denver and Albuquerque have what has been termed a wintertime "brown cloud" problem (see Fig. 5). Ten years ago some scientists speculated that the haze was caused by wind-blown dust. More recent wintertime studies by Wolff *et al.* (1981) have shown that in Denver the haze results principally from fine particles. In the studies by Wolff *et al.* (1981) and by Lewis and Einfeld (1985), the "brown cloud" of Denver in the winter resulted mainly from carbon, sulfate, and nitrate, which are found in the fine fraction ($< 2.5\ \mu m$).

Because of the geographic and socioeconomic similarity between the two cities, the data in Table 2 can be used to illustrate how a simple receptor modeling calculation from a few air samples can assist in determining the relative contributions of local emission sources on air quality. For example, in the case of the data set for Albuquerque, we see that the nighttime potassium concentration in the fine particles was 5 times higher than that in the daytime period. In addition, the total carbon concentration in the nighttime period was 4.5 times higher ($90\ \mu g/m^3$) than in the daytime sample. On the other hand, the lead concentrations in the fine particles were approximately the same ($\sim 1.0\ \mu g/m^3$) for both the day and night samples and indicate, to a first approximation, that the carbon contribution from mobile vehicles was about the same for the two sampling periods.

From the studies performed by DeCesar and Cooper (1982) and Stiles (1983), we conclude potassium was ap-

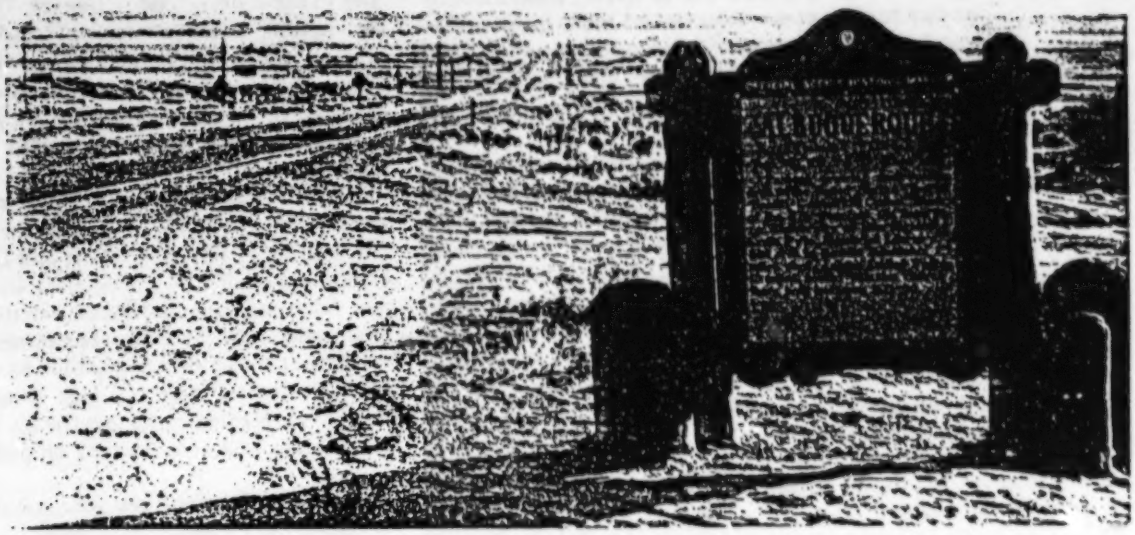

Fig. 5. Albuquerque winter haze.

proximately 1% of the fine particle emissions from pine wood burning. Note that in Albuquerque most of the wood burned is of a pine variety, principally mesquite. The ratio of potassium to fine particle emissions from wood burning of different types of wood is an area that requires considerably more research to establish emission rates for a variety of woods and to determine the range of uncertainty in these emission measurements. Since the potassium concentration at night in the fine particle sample was 0.61 $\mu g/m^3$, the total fine particle mass from wood burning that would accompany the potassium would be the ratio: $0.61 \div 0.01 = 61\ \mu g/m^3$. This calculation assumes that all the potassium in the fine fraction originates from wood burning, and the pathways for transport of the potassium and associated mass from wood burning are identical. Another assumption is that most wood burning occurs at night. This assumption is reasonable, based on the habits of most individuals who use would stoves or fireplaces and on the results obtained by a survey performed by Dennis (1983).

Thus, based on this simple calculation and these assumptions, 61 $\mu g/m^3$ of the 154 $\mu g/m^3$ is probably due to wood burning. About 80% of the fine particles from wood burning are in the form of carbon (Cooper and Malek, 1982; Kleinman *et al.* 1980). Therefore, for this sampling period 52 $\mu g/m^3$ of the total carbon appears to be from wood burning. Multivariate analyses of the Albuquerque data set performed by Sandia Laboratories, indicate the balance of the total carbon in this fine particles sample from Albuquerque appear to be from motor vehicles.

This crude calculation can be refined by using the elemental composition obtained from both the fine and coarse particles. In airsheds where coarse particles are likely to be abundant, it is essential that the K used as a tracer for wood burning be in the fine fraction and corrected for soil-derived K. This is necessary because K is often abundant in the soil, and the amount of soil suspended as particles is dependent on meteorological conditions. During windy days most of the soil particles are present in the coarse fraction, but some enrichment of the soil-derived particles occurs in the fine fraction. For this reason, a correction for the K from the soil-derived particles must be made to deduce the K from wood burning alone. This correction is described by Lewis and Einfeld (1985).

An alternative, and perhaps a more accurate means of determining the K concentration in the fine fraction that is due to soil particles, is to analyze the fine soil particles for elemental composition. This can be accomplished by (1) obtaining a soil sample from the airshed under study

(preferably a soil sample near the sampling site), (2) resuspending the soil and sample suspension into a dichotomous sampler, (3) collecting the sample onto a Teflon filter, and (4) analyzing the sample and determining the K-to-Fe ratio. The excess K over K-to-Fe ratio of soil can then be assumed to be from wood burning. This, of course, assumes that there are no other sources of K.

In certain geographic areas, air quality measurements are not so clear as the observations made in Albuquerque. In those cases, a larger number of aerosol samples from ambient air and point sources may need to be collected to determine the contributions of sources to fine particles.

In contrast to Albuquerque, the analysis of the aerosols collected in January 1982 in Denver was considerably more complicated. The calculations were more complicated because the soil in Denver is rich in K, which makes the apportionment of carbon emissions from wood stoves using potassium, the tracer, dependent on knowledge of the soil compositions. In addition, the mass of fine particles during the study never exceeded 42 $\mu g/m^3$, and the total carbon concentrations did not exceed 31 $\mu g/m^3$. These concentrations were substantially lower than those observed in Albuquerque. Therefore, in order to perform a viable source apportionment determination, the procedure of Kleinman *et al.* (1980) was used to calculate the origins of the fine particles. This receptor modeling procedure is based on an initital factor analysis of a set of elemental composition measurements from a minimum of 30 observations (Lewis and Einfeld, 1985). With the single element tracers identified in this step, a stepwise, multiple linear regression then determines the percentages impact of the sources associated with those tracers.

The results of this source apportionment calculation are shown in Table 3. Details of the source apportionment study performed in Denver are described by Lewis and Einfeld (1985).

In Denver during January 1982, wood burning appeared to contribute 6% to the fine particle mass. This apportionment is dependent on the key assumption that the corrected fine particle K concentration is due entirely to wood burning. The factor analysis indicates a portion of the K is not from soil and the K was not correlated with the sulfate and nitrate. Also, K is one of the major elements emitted from wood burning. Therefore, it is not unreasonable to make the assignment cited in Table 2. Assuming the mass is to be proportional to the total extinction coefficient (Hasan and Dzubay, 1983), then wood burning does not appear to be a significant contributor to the brown cloud in Denver. This is a reasonable assumption, since the elemental carbon, the light-absorbing species, was less than 5% of fine particles mass. However, this assertion is further based on the assumption that the receptor site where the particles were collected was representative of air quality over metropolitan Denver.

Based on the emissions inventory/dispersion approach, Dennis (1983) speculates the Denver receptor site used by Wolff *et al.* (1981) and Lewis and Einfeld (1985) was located in a section of Denver where there was relatively little residential wood-burning activity. Additional ambient air measurements in Denver are needed to confirm this speculation. Measurements in urban areas where there is a high density of residential homes are recommended by Dennis to observe maximum impact of wood burning on particulate mass.

Table 3. Denver source apportionment of wintertime fine particle composition (January 1982).

Sources	Average Impact ($\mu g/m^3$)	Tracer Species	%
Mobile sources	9.2 ± 1.5	Pb	44
Power plants	5.9 ± 1.1	SO_4^{2-}	28
Crustal	1.7 ± 2.7	Si	8
Wood burning	1.3 ± 0.5	K[b]	6
Other (intercept)	2.7		13
Calculated	20.8		
Measured	20.1		

[a]Tracer species identified from factor analysis of data set.
[b]K concentration for soil contribution to fine particle K.

Ambient Air Sampling and Analysis Procedures in Support of Receptor Modeling

Table 4 contains a list of air quality measurements in order of priority needed to determine the amounts of pollutants in ambient air that result from wood burning. The two dichotomous samplers listed in Table 4 (or two samplers equipped with a cyclone separator that can collect fine particles) are needed to obtain the air quality measurements for the source apportionment calculations. One sampler will collect the fine particles on Teflon filters and the other sampler will simultaneously collect the particles on quartz filters. The volatile and elemental carbon measurement will be obtained from the samples collected on the quartz filters. The mass, elemental composition, and light-absorption coefficient β_{abs} of the aerosols are obtained from the samples collected on the Teflon filters.

Mass and β_{abs} measurement. The fine particle mass measurements are useful because visual range can be estimated using the following equation, which was deduced by Stevens *et al.* (1984) for the case where the particle scattering is the dominant contributor to visibility degradation:

$$\text{Visual range (km)} = 0.42 \div \text{fine particle mass (mg/m}^3\text{)}. \quad (3)$$

This equation implies that for a fine particle mass loading of 84 $\mu g/m^3$ (0.084 mg/m^3), the visual range will be 5 km. A similar result was obtained by an independent method (Stevens *et al.*, 1983). The β_{abs} measure-

Table 4. Air quality measurements to support receptor modeling related to wood burning emissions.

Sampling or Monitoring Procedure	Chemical Species Monitored	Monitoring Frequency	Analytical Procedure	Reference
Dichotomous sampler with Teflon 2-μm pore size; 37-mm diam. filters, Membrana Corp. Pleasanton, CA	1) Fine particle		Gravimetric	Shaw *et al.* (1980) Courtney *et al.* (1982)
	2) Elemental	12 h	XRFA[a]	Stevens *et al.* (1978)
	3) B_{abs}[b]		Light transmission	Stevens *et al.* (1982)
	4) Sulfate and nitrate		Ion exchange chromatography	Stevens *et al.* (1978)
Dichotomous sampler with quartz, 37-mm diam. filters	5) Elemental carbon (C_e), condensable organic carbon species (C_{oc})	12 h	Combustion	Stevens *et al.* (1982) Cadle *et al.* (1981)
Nondispersive-infrared monitor	6) CO[c]	1-h averages	Optical	
Integrating nephelometer	7) Particle scattering	real time	Light scattering due to fine particles	Dzubay *et al.* (1982)
High-volume samplers equipped with impactor to remove particles >2.5 μm; quartz filters	$^{14}C/^{12}C$ radio isotopic measurements on bulk sample and organic compounds	12 h	Linear accelerator	Currie *et al.* (1983)

[a]XRFA = X-ray fluorescence analysis.
[b]β_{abs} = a measurement of the amount of visible light absorbed by aerosols collected on a thin membrane filter. The amount of visible light absorbed by the particles on the filter is generally correlated with the mass of soot carbon present in the sample.

ments are useful since they are highly correlated with the mass of fine black soot carbon collected on Teflon filters (Stevens *et al.*, 1982). This measurement from Teflon filters may be used in place of carbon measurements from quartz filters in field studies where only samples collected on Teflon were obtained.

Elemental Composition. The elemental composition (principally of the elements potassium, lead, and bromine) is typically used in conventional receptor model calculations to differentiate the impact of wood burning emissions from auto exhaust emissions. (Dzubay *et al.*, 1984, have prepared a useful list of elements that can be used in receptor models to assess the impact of a variety of industrial sources). Potassium is the tracer element for wood-smoke emissions, while lead and bromine are used to calculate the impact of mobile vehicles on particle mass.

Carbon Measurements. Stevens *et al.* (1978) have documented the basis for using Teflon filter substrates to obtain mass measurements and perform XRF analyses for elemental composition. However, carbon measurements are not easily obtained from Teflon filters, since the procedure used most frequently to measure carbon in aerosols is based on high-temperature combustion methods. For this reason, a second fine particle sample must be collected on quartz at the same time the aerosols are being collected on Teflon. Quartz is used as the collection medium because it has a low carbon content, high collection efficiency, and is chemically inert. An aliquot of the quartz filter can be analyzed by a combustion procedure similar to one described by Stevens *et al.* (1982). This procedure measures volatile carbon and elemental carbon from the same sample.

Recent comparisons of methods (Cadle *et al.*, 1981) to measure elemental, total, and volatile carbon content of aerosols indicate that procedures that depend on combustion or pyrolysis to convert the carbon species into methane followed by flame ionization measurement, may produce substantially different, results, depending on the conditions of combustion. For example, to convert completely all the aerosol carbon on quartz filters requires a temperature of at least 850 °C and the presence of oxygen in the helium carrier gas. Without oxygen, a substantial amount of elemental carbon will not be pyrolyzed and consequently not be measured.

For the results presented in this paper, the elemental and condensable carbon present in ambient particulate samples are measured using a modified Dohrmann DC-50 organic analyzer. Figure 6 is a diagram depicting the sample introduction, pyrolysis, combustion, and detector assemblies. The DC-50 measures the organic carbon (condensable organic compounds) by pyrolyzing the carbonaceous portion of the sample at 650 °C in a helium atmosphere to CO_2 and other pyrolysis products, reducing the products to methane over a bed of nickel catalyst in an atmosphere of hydrogen, and measuring the methane with a flame ionization detector. After the organic analysis, elemental carbon is determined by combustion of the carbonaceous materials re-

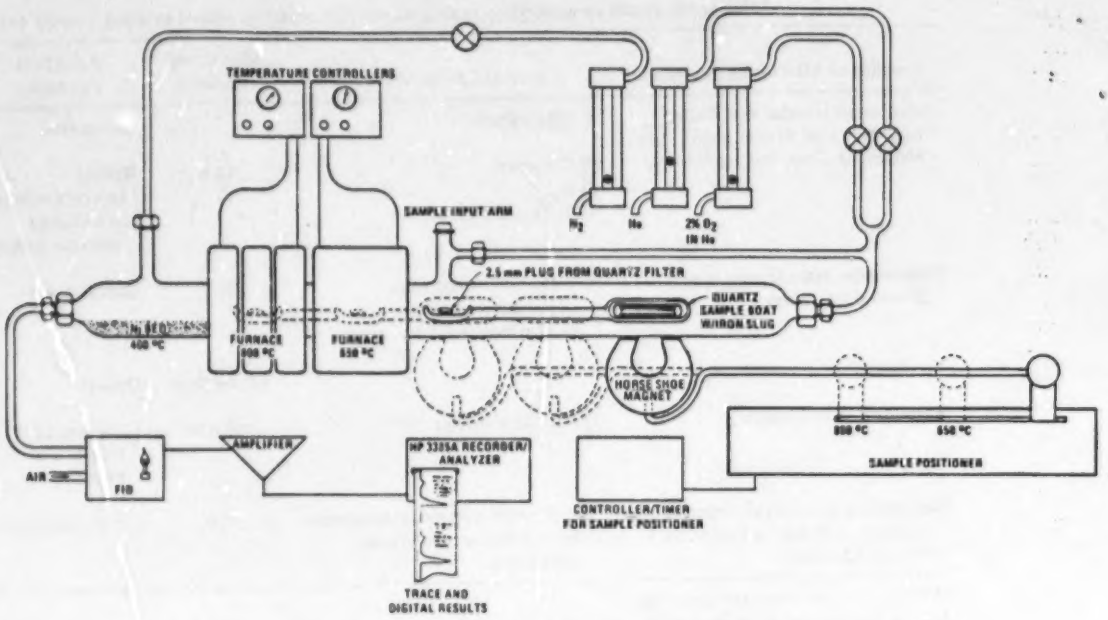

Fig. 6. Diagram of modified Dohrmann DC-50 carbon analyzer.

maining on the quartz filter at 850 °C in a 2% oxygen, 98% helium atmosphere. Total carbon is considered to be the sum of the organic and elemental analysis. Recently, the procedure to collect fine particles on quartz filters has been modified to minimize the variation in blank mentioned above. The modification reduces the deposit area of the sample from 37 mm to 13 mm, as shown in Fig. 7. This focusing of the sample to a 13-mm area reduces the impact of the carbon blank, and the area outside of the deposit area becomes the blank for that filter. The combination of increased sample per unit area and a blank for each sample should improve the precision of the combustion procedure to determine carbon content of aerosols.

Sulfate, Nitrate, and Particle Scattering. The last analysis necessary to account for all the fine particle mass consists of ion exchange measurements for sulfates

Fig. 7. Fine particle samples collected on quartz filters. Sample A was collected by modifying sample flow to focus aerosols into a 13-mm spot. This provides a high density of sample per unit area and reduces a blank uncertainties. Sample B collected normally in Denver, CO, in January 1982. The holes in the filters are where pieces are removed for carbon analysis.

and nitrates. Stevens *et al.* (1978) describe in detail the extraction and ion exchange analysis for the anions and cations present in ambient particles.

The integrating nephelometer measures the light scattering of fine particles. Therefore, during periods when wood burning is most prevalent (namely, nighttime during the winter), increases in the ambient fine particles would also register a signal from the integrating nephelometer. Measurements by the nephelometer would also serve as an input to the receptor model calculation. The carbon monoxide and lead measurements would also assist in determining the impact of wood burning or auto exhaust emission on air quality through correlation matrix calculations that include the broad range of measurements discussed above and listed in Table 4. After completion of all the analyses described above, a data set is available for a variety of source apportionment calculations.

Special Studies Associated with Ambient and Source Sampling to Determine Sources of Ambient Carbon Species

Organic compounds present in primary particles from sources such as oil refineries and mobile vehicles would seem to be ideal candidates for tracers in receptor modeling studies. Certain polynuclear aromatic hydrocarbons (PAHs), for example, in fine ambient air particles from these sources may serve as a tracer species for certain sources. However, they have not been used extensively as tracers because the chemical analysis required for PAHs is complicated and expensive. In airsheds where there are multiple sources of carbon aerosols, though, the use of organic tracers may be the only way to obtain the resolution of the sources contributing to the ambient particulate burden (Gordon *et al.*, 1984). According to available literature as interpreted by Chaung (1983), cyclopenta(*c,d*)pyrene is high in gasoline emissions, but low in diesel exhaust, while benzo(*g,h,i*)-perylene and coronene are high in diesel exhaust. This information, combined with carbon monoxide, lead, and vanadium data, may serve as an indication for mobile and nonmobile sources of fine particle carbon and assist in performing a reliable source apportionment.

Table 5 lists organic species that may be candidates for receptor modeling calculations to differentiate between the impact of the principal sources of carbon on urban atmospheres.

The two chromatograms in Figures 8a and 8b show several organic species that could serve as tracers for wood burning. Chromatogram I is from the gas chromatography (GC) analysis of a gas chromatographic/mass spectrometric (GC/MS) analysis of a methylene chloride extract of a wood-stove emission, collected from a private residence in Muscle Shoals, AL, with the S[2] samples of Stiles (1983), described earlier in this report. Chromatogram II is a GC analysis of a methylene chloride extract from an ambient fine particle sample collected in Muscle Shoals, AL, concurrently with the source sample. This preliminary GC study indicates that several organic species are common to both samples. Table 5 lists those oxidized organics observed in the GC analysis that may be candidates for receptor modeling of wood-burning emissions. These compounds, because of their oxygenated characteristics, would be expected from the pyrolysis of wood products. Additional research is required in this area to quantitatively

Table 5. Organic compounds present in wood burning and mobile sources that could be used in receptor modeling (Chaung, 1983).

Wood Burning	Mobile Sources
Methoxyanisole ($C_8H_{10}O_2$)	Cyclopenta(*c,d*)pyrene($C_{18}H_{10}$)
Vanillic acid ($C_8H_{12}O_3$)	Benzo(*g,h,i*)perylene($C_{22}H_{12}$)
Methoxyhydrobenzoic acid ($C_9H_{12}O_3$)	Coronene ($C_{12}H_{12}$)
Syringaldehyde ($C_{11}H_{14}O_3$)	Pyrene ($C_{16}H_{10}$)
Isomers of ($C_{10}H_{14}O_3$)	

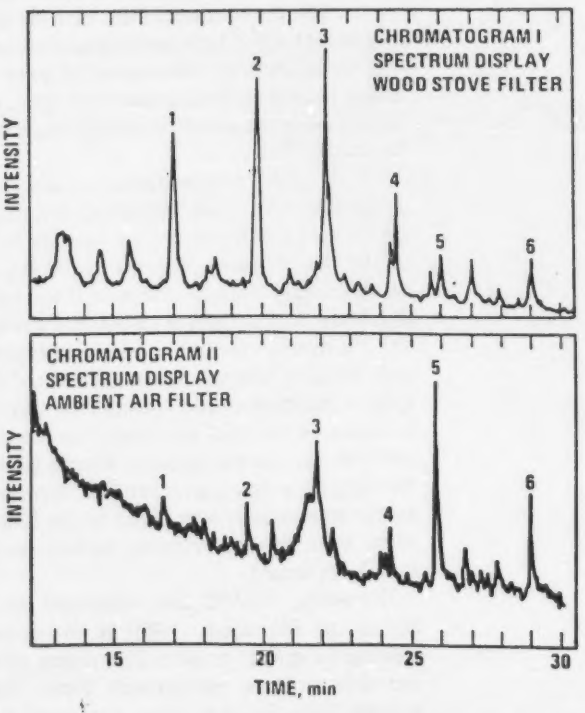

Fig. 8. Plots of gas chromatography/mass spectrometry (GC/MS) data. (a) Data from source-signature sampler quartz filter: (1) $C_8H_{10}O_2$, methoxyanisole, or dimethylemelanine; (2) vanillic acid, methoxyhydroxybenzoic acid, or $C_9H_{12}O_3$. (3) $C_{10}H_{14}O_3$ (isomers); (4) $C_{10}H_{14}O_2$ (isomers) or $C_{13}H_{16}$ (isomers); (5) $C_{11}H_{14}O_3$ or syringaaldehyde; (6) $C_{12}H_{16}O_2$ or $C_{16}H_{10}$. (b) Data from Sierra sampler quartz filter: (1) $C_8H_{10}O_2$, methoxyanisole, or dimethylemelanine; (2) vanillic acid, methoxyhydroxybenzoic acid, or $C_9H_{12}O_3$; (3) $C_{10}H_{14}O_3$ (isomers); (4) $C_{10}H_{14}O_2$ (isomers) or $C_{13}H_{16}$ (isomers); (5) $C_{11}H_{14}O_3$ or syringaaldehyde; (6) $C_{12}H_{16}O_2$ or $C_{16}H_{10}$.

relate these concentrations of organic compounds to the fine particle mass and carbon from wood burning before these species can be used in receptor models.

Khalil *et al.* (1983) have recently described a novel method in which methylchloride (CH_3Cl), a low-temperature pyrolysis product from wood, is used as a tracer to measure the contributions of wood burning to urban air pollution. Khalil claims the method can measure in near real time the mass of fine particles from wood burning through the following relationship:

$$C_s(\mu g/m^3) \cong 0.6\Delta C_g(\text{pptV}), \quad (4)$$

where C_g(pptV) = parts per trillion (nL/L) by volume of CH_3Cl in ambient air, and
$C_s(\mu g/m^3)$ = mass of fine particles from wood burning.

According to Khalil *et al.* (1983), the uncertainties in determining the mass in $\mu g/m^3$ of fine particles from wood burning with the tracer methylchloride in the above cited equation are largely due to the variability of the ambient background concentrations of CH_3Cl and the difficulty of obtaining accurate emission measurements. The authors state that, because of the variability of ambient CH_3Cl concentrations (urban concentration non-wood-burning periods $\cong$500 pptV or nL/L), the model is unlikely to provide estimates of wood burning contributions to ambient particle mass loadings of better than $\pm$50%.

Currie (1982) determined the relative amounts of particulate carbon from contemporary (e.g., wood) and fossil fuel carbon combustion sources by means of data on the $^{14}C/^{12}C$ ratio. The distinction is possible because contemporary carbon contains trace amounts of ^{14}C, but fossil fuel carbon is essentially devoid of ^{14}C. The $^{14}C/^{12}C$ measurements are relatively expensive, and only two or three laboratories in the United States are capable of performing the analysis. In addition, milligram amounts of material are needed to measure $^{14}C/^{12}C$ in ambient particulate samples. Currie (1983) is currently working on a new procedure that measures ^{14}C with an accelerator mass spectrometer at the University of Arizona. With this new system, as little as 100 μg carbon may be analyzed.

Normally, $^{14}C/^{12}C$ are measured at the National Bureau of Standards (NBS) in Washington, DC, by heating the quartz or glass fiber filters to distill the condensable organic compounds from the filters; the organic compounds are then converted to CO_2 and the CO_2 condensed into a glass micro cell. The cell is placed into a sealed chamber and the radioactivity measured with a sensitive proportional counter. Recently, Stevens *et al.* (1984) reported the presence of carbonates, acetate, and formate in aqueous extracts of ambient fine particles collected in the Shenandoah Valley. Stevens *et al.* (1984) postulated these species may interfere with ^{14}C measurements, since the carbonate may be due to CO_2 being adsorbed onto the quartz filter. Since almost all of the ambient CO_2 is rich in ^{14}C, the bulk ^{14}C analysis described above may be influenced by the CO_2 artifact formed with the quartz filter.

For this reason, the improved ^{14}C method described by Currie (1982) could be modified to eliminate this problem through an additional step of organic extraction of the ambient sample prior to ^{14}C analysis. This extraction step would all but eliminate the interference due to adsorbed gases (CO_2) on the quartz filters, since they would be lost during the evaporation of the solvent after the filter has been extracted. In addition, measurement of the ^{14}C content of the major classes of condensable organics is now possible and could enhance the range of species used in receptor models. Another possibility for eliminating the artifact influence would be by fractional distillation of the organics from the filter, followed by ^{14}C analysis of the individual thermally released organics. We would expect that only the fraction initially evolved from the filter would contain most of the artifactual ^{14}C.

Conclusion

The source apportionment sampling and analysis protocol presented in this report should be considered dynamic and subject to revisions as we learn more about the organic and inorganic emission characteristics of wood burning. In some source apportionment studies, a substantial amount of resources may be expended in obtaining source signatures, if there are sources of carbon other than motor vehicles and wood burning. In some urban areas, more than one receptor site may be needed to collect ambient particles, if the location of the sources responsible for the fine particles produce pockets of pollution within the airshed. The important feature of the protocol presented in this report is its use of existing sampling and analysis methods, which have been well documented and are being used in a variety of urban aerosol characterization programs to determine the impact of wood burning on ambient air particulate matter loadings.

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